Fe$_3$BO$_5$@carbon core–shell urchin-like structures prepared via a one-step co-pyrolysis method

Zhongchao Bai, Zhicheng Ju, Liancheng Wang, Bo Sun, Changhui Sun, Liqiang Xu *, Yitai Qian

Key Laboratory of the Colloid and Interface Chemistry (Shandong University), Ministry of Education, and School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

ARTICLE INFO

Article history:
Received 27 February 2011
Accepted 10 May 2011
Available online 13 May 2011

Keywords:
Carbon materials
Composite materials
Nanocrystalline materials

ABSTRACT

Urchin-like Fe$_3$BO$_5$@carbon core–shell structures (defined as “FBOC”) have been fabricated by a one-step co-pyrolysis method using boric acid and ferrocene as raw materials. This complex architecture is composed of high-density Fe$_3$BO$_5$@carbon nanocables that stand on Fe$_3$BO$_5$@carbon structure. After removing the Fe$_3$BO$_5$, hollow urchin-like carbon material was obtained. In the reaction process, B$_2$O$_3$ and H$_2$O that decomposed from H$_2$BO$_3$ have synergistic effect on the formation of urchin-like structures. It is found that urchin-like structures can also be obtained when other materials that can release H$_2$O and B$_2$O$_3$ react with ferrocene. The influences of the reaction conditions on the preparation of FBOC have been discussed in detail.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Ferroferraborate (Fe$_3$BO$_5$), as a mixed valence compound, displays many interesting properties, such as catalytic oxidation of small organic molecules (ethyl acetate and methanol) [1,2], paramagnetic–antiferromagnetic transition at 114 K and a charge ordering crossover at 220 K [3,4]. It could also be applied as stuff in studies of the mechanisms of electron interactions in transition metal oxides.

Nanoscale Fe$_3$BO$_5$ are apt to be agglomerate, and their structures are easily collapsed even in a mild reducing atmosphere at 500 °C, which would hinder their wide applications. Surface modification is considered to be an effective way to prevent the agglomeration. Fe$_3$BO$_5$ nanorods coated with silica composite have been produced, their morphology and performance were well remained even after high temperature treatment [5]. Besides silica, amorphous carbon has also been widely used as a protective material to improve the corrosion resistance, thermal stability, adsorbability, or electronic properties of the materials such as polymers, ceramics, metals, and oxides [6].

As is known that ferrocene could easily decompose into Fe nuclei and carbon species at relatively low temperature (≥500 °C), therefore, ferrocene has been widely used for the synthesis of carbon materials such as CNTs, hollow carbon spheres, carbon encapsulates, and iron-related carbon composite materials [7–10]. In this experiment, ferrocene and boric acid were used as raw materials for the synthesis of FBOC. The average size of the prepared FBOC is 3 μm. In addition, hollow urchin-like carbon materials were obtained after the inside Fe$_3$BO$_5$ were removed by HCl at 80 °C for 5 h. This kind of FBOC may offer an opportunity to investigate the magnetic and catalytic properties of the composites, and the hollow carbon materials may be used as templates to synthesize other kinds of urchin-like materials or composites.

2. Experimental section

All the chemical regents used here were analytical grade. In a typical procedure, ferrocene (0.005 mol, 0.932 g) and boric acid (0.01 mol, 0.632 g) were put into a stainless steel autoclave of 20 ml capacity. The autoclave was sealed and loaded into an electronic furnace at 150 °C, and then the temperature of the furnace was increased to 600 °C at the rate of 10 °C/min and maintained at 600 °C for 10 h before being air-cooled to room temperature. It was found that the final product in the autoclave was black powder. The black powder was collected and divided into two parts: one part was washed with distilled water and absolute ethanol several times to obtain the urchin-like Fe$_3$BO$_5$@carbon core–shell nanostructure material; the other part was heated in dilute HCl solution at 80 °C for 5 h to obtain hollow urchin-like carbon material. After that, the two samples were dried in a vacuum box at 60 °C for 10 h and collected for characterization. Microstructure and phase structure were characterized with SEM, HRTEM, XRD and TEM techniques.

3. Results and discussion

Fig. 1a and b shows the X-ray powder diffraction (XRD) patterns of the FBOC before and after acid treatment, respectively. According to Fig. 1a, all the distinguished diffraction peaks can be indexed as Fe$_3$BO$_5$ (JCPDS Card No. 25-0395). Fig. 1b shows the XRD pattern of
the product after heated in diluted HCl solutions, which can be attributed to carbon materials. Fig. 2 shows the Raman spectrum of FBOC after HCl acid treatment. There are two obvious peaks at 1340 and 1600 cm\(^{-1}\). The peak at 1600 cm\(^{-1}\) (G-band) can be indexed as the stretching modes of C=C bonds of graphite, while the peak centered at 1340 cm\(^{-1}\) (D-band) corresponds to the vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite [11]. These results completely prove that the as-obtained products are carbon materials.

The thermal stability of the as-obtained sample was studied by TGA (ESI-Fig. 1). The result indicates that below 440 °C the product is stable in ambient atmosphere, which can be attributed to the protection of outside carbon shells. From the TGA curve, one can observe that a rapid weight loss emerged in the temperature range of 440–620 °C, and this result is closed to that of the previous reports of carbon [12].

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) observations indicate that the products are composed of a large quantity of urchin-like structures with average size of 3 μm. Fig. 3 shows typical TEM and SEM images of the as-obtained FBOC. These FBOC are composed of spheres and cables: spheres act as the cores and Fe\(_3\)BO\(_5@\)carbon nanocables as the surrounding spines (Fig. 3a). Most of those “spines” are Fe\(_3\)BO\(_5@\)carbon nanocables. Fig. 3b shows a close observation of nanocables. The distinct contrast suggests their core–shell nanostructural features. The surfaces of the shells are smooth and 11 nm thick. The lengths of the nanocables are ranging from 50 to 950 nm. The HRTEM analysis offers more detailed information of the Fe\(_3\)BO\(_5@\)nanowires (Fig. 3c). The lattice fringe observed in this image is 0.51 nm, which corresponds to the interplanar spacing of the (200) plane of Fe\(_3\)BO\(_5@\). This is consistent with the previous report of the plywood-like Fe\(_3\)BO\(_5@\)nanorods [13]. After acid treatment, hollow carbon materials were obtained as shown in Fig. 3d. The morphology and size of the hollow carbon materials were the same as the FBOC.

The panoramic morphology of FBOC architectures shown in Fig. 3e reveals that the samples have urchin-like shapes with an average size of 3 μm, which agrees with the TEM observations. The magnified view of an individual FBOC clearly reveals the exact configuration about the FBOC (Fig. 3f). It is found that some of the “spines” were broken, which may be caused by ultrasonic process during the preparation of the SEM sample.

A series of contrast experiments were carried out through similar processes to investigate the effects of reaction parameters (i.e., reaction temperature, reaction time, and boron source.) on the formation of FBOC. Keeping other conditions unchanged, when boric acid was replaced by equimolar amount of other borates, such as ammonium tetraborate hydrate, magnesium metaborate, sodium tetraborate decahydrate and lithium tetraborate, we discovered that only ammonium tetraborate hydrate could produce urchin-like structure materials. The reason may be that ammonium tetraborate hydrate as well as boric acid can easily decompose and release B\(_2\)O\(_3\) and H\(_2\)O. The released B\(_2\)O\(_3\) and H\(_2\)O might play crucial roles during the formation of urchin-like Fe\(_3\)BO\(_5@\). It is also proved by the fact that when the same amounts of B\(_2\)O\(_3\), H\(_2\)O and ferrocene were used as the initial material, urchin-like structure materials were also obtained. But if only B\(_2\)O\(_3\) or H\(_2\)O reacted with ferrocene, urchin-like structure could not be gained. Therefore, we can reasonably conclude that B\(_2\)O\(_3\) and H\(_2\)O have synergistic effect on the formation of FBOC. The reaction temperature is another determining factor on the formation of FBOC. If the reaction temperature was set at 500 °C, a mixture of the ball-like structures with nanorod bundles, and branched cables was observed (ESI-Fig. 2a). When the reaction temperature was set at 700 °C, the proportion of urchin-like structures was reduced while branch-like structures were detected (ESI-Fig. 2b). When reducing the reaction time, FBOC co-existing with particles were observed; if prolonging reaction time, no significant difference on the structures was found. Hereby, 600 °C and 10 h are the optimal parameters for the production of FBOC.

According to the above results and analysis, the possible formation mechanism of FBOC was proposed. It is well known that both ferrocene and H\(_2\)BO\(_3@\) are readily decomposed with increasing temperature and release Fe, H\(_2\)O and B\(_2\)O\(_3\) respectively. A part of the Fe atoms would react with H\(_2\)O to form Fe\(_2\)O\(_3\) nuclei, and then the remaining Fe, H\(_2\)O and B\(_2\)O\(_3\) would interact and form Fe\(_3\)BO\(_5\) nanowire on the Fe\(_2\)O\(_3\) nuclei. This process is similar with the previous report about the preparation of Fe\(_3\)BO\(_5\) nanorods [5]. At the end of this experiment, ferrocene was converted into Fe\(_3\)BO\(_5\), C and residual gasses. It is reasonable to speculate that carbon atoms are coated on the surface of the Fe\(_3\)BO\(_5\) to diminish the surface energy. However, the exact formation mechanism of the as-obtained FBOC still needs further research.

4. Conclusions

In this study, we have successfully synthesized FBOC with high yield by the pyrolysis of ferrocene and boric acid mixture in a stainless steel autoclave. After HCl treatment, hollow urchin-like carbon materials were obtained. Their size and structure were studied by SEM, TEM and HRTEM. The XRD and Raman spectra confirmed that both FBOC and hollow urchin-like carbon materials exhibit high purity. Furthermore, this kind of FBOC may offer an opportunity to
investigate dimensionally confined systems, and the hollow carbon material may be used as template to synthesize other kinds of urchin-like materials.

Acknowledgment
This work was supported by the National Nature Science Foundations of China (Grant Nos. 20871075 and 20971079), the 973 Project of China (No. 2011CB935901), and the Independent Innovation Foundations of Shandong University (2009TS017, 2009JC019, and yzc10092).

Appendix A. Supplementary data
Supplementary data to this article can be found online at doi:10.1016/j.matlet.2011.05.039.

References

Fig. 3. Low-magnification (a) and high-magnification (b) TEM images of FBOC. (c) HRTEM image of the Fe3BO5. (d) Low-magnification of the hollow carbon materials. (e) The SEM images of FBOC and (f) single FBOC prepared at 600 °C.

Z. Bai et al. / Materials Letters 65 (2011) 2479–2481